

SIR WYNDHAM ROWLAND DUNSTAN

1861—1949

BY

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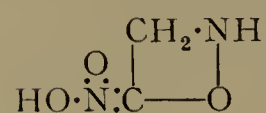
1861—1949.

SIR WYNDHAM ROWLAND DUNSTAN, K.C.M.G., LL.D., F.R.S., died on April 20th, 1949, at the age of 87. He was the son of John Dunstan, Constable and Governor of Chester Castle, and was born at Chester on the 24th May, 1861. He was educated at Bedford School and abroad and began his chemical career at the early age of 18 by becoming assistant to Theophilus Redwood, then Professor of Chemistry at the School of Pharmacy of the Pharmaceutical Society. When this post was divided by the allocation of laboratory work to Professor John Attfield, Dunstan became a demonstrator under Attfield. In 1884 he moved to Oxford having been appointed a demonstrator in the University Chemical Laboratories, and in the following year he was made University Lecturer in Chemistry in Relation to Medicine, a post he retained for some years after succeeding Redwood as Professor of Chemistry in the Pharmaceutical Society's School in 1886. From 1892 to 1900 he was also lecturer in chemistry at St. Thomas's Hospital Medical School, a post he kept for four years after his appointment as Director of the Scientific and Technical Department of the Imperial Institute in 1896. Seven years later he succeeded Sir Frederick Abel in the full Directorship of the Institute, where he remained until his retirement from active work in 1924.

Dunstan's early work was concerned almost wholly with the development of processes for the assay of active components in the natural drugs of the British Pharmacopoeia, and with the application of the results to the production of galenical preparations of these drugs, such as tinctures and extracts, in a standardised form, *i.e.*, containing a specified percentage of the active substance. This was due to the fact that the 1874 Pharmacopoeia was then under revision, Redwood being one of the responsible editors, and the necessary experimental work had to be done in his laboratory. Dunstan had a practical bent of mind well suited to such investigations, as is shown by his work on *nux vomica* with F. W. Short and on solanaceous drugs with F. Ransom and A. E. Chaston. Nine papers were published on *nux vomica* of which the most interesting are probably that on the isolation of the crystalline glucoside, loganin, from the pulp of *nux vomica* fruit (*Pharm. J.*, 1884, [iii], 14, 1025) and that dealing with the quantitative separation of strychnine and brucine, based on the precipitation of the former as ferrocyanide and recovery of the alkaloid, as adopted in the Pharmacopoeia of 1898. Four papers on the assay of alkaloids in belladonna leaves and root and on the standardisation of their preparations were published by Dunstan and Ransom (*ibid.*, 1884, [iii], 14, 623; 1884, [iii], 15, 154; 1885—6, [iii], 16, 237, 777; 1887, [iii], 17, 843), and special attention was given to the rhizome of *Scopola carniolica* from which Dunstan and Chaston isolated hyoscyamine, possibly a minute amount of hyoscyne, a phytosterol, arachidic acid from the fat, dextrose, and scopoletin (*ibid.*, 1889, [iii], 20, 461). This drug was at that time regarded as a possible substitute for belladonna, and a group of workers published papers on it: E. M. Holmes on its natural history; T. Greenish on the histology; F. Ransom on its pharmacy; and Sir Dyce Duckworth on the therapeutic action (*ibid.*, pp. 468, 471, 464, 466).

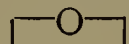
Dunstan also set out to improve the two alkyl nitrite preparations of the Pharmacopoeia and to that end prepared in collaboration with T. S. Dymond, E. J. Woolley, and W. Lloyd Williams (*ibid.*, 1888, [iii], 18, 861; 19, 485, 487, 489, 741) the homologous series from methyl to *n*-, *sec*-, and *tert*-amyl nitrites, which were examined pharmacologically by Professor J. T. Cash, who, in addition to a number of conclusions which have since become familiar features of pharmacological action in homologous series, showed that the action of the nitrites is not solely, or even mainly in some cases, caused by the amount of nitroxyl (NO_2) they contain, and suggested that the simple nitrites attached themselves more readily to certain constituents of blood and muscle and so acted more quickly, whilst their greater stability ensured longer duration of action

(Cash and Dunstan, *Phil. Trans.*, 1893, B, **184**, 505). A side issue of this work was the observation by Dunstan and Dymond (*Proc. Chem. Soc.*, 1888, 117; *J.*, 1891, **59**, 410) that the action of alkali on nitroethane produces acetonitrile, nitrous acid, and 3 : 4 : 5-trimethylisooxazole, the last a type of compound first prepared by Claisen and Lowman (*Ber.*, 1888, **21**, 18, 1149). With nitromethane, alkalis produce, not an isooxazole, but methazonic acid, $C_2H_4O_3N_2$, a substance first obtained by Lecco (*Ber.*, 1876, **9**, 705). It was prepared and examined by Dunstan and Goulding (*J.*, 1900, **77**, 1262) who, mainly on the ground that on hydrolysis by alkali or acid it



produced carbon dioxide, hydroxylamine, and hydrocyanic acid, proposed for it the annexed formula, but shortly afterwards Scholl (*Ber.*, 1901, **34**, 862) suggested that it might be regarded as a nitrogen analogue of acetoacetic acid and formulated as $\text{CH}_2\cdot\text{NO}\cdot\text{CH}\cdot\text{NO}\cdot\text{OH}$, and later Meister (*Ber.*, 1907, **40**, 3435) recorded a number of new reactions for the acid and claimed that it could be represented as $\text{HON}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{NO}_2$, or as its conjugated tautomeride $\text{HO}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{NO}\cdot\text{OH}$.

About this time the long-continued discussion on the isomerism of aldoximes was beginning and Dunstan and Dymond showed that acetaldoxime, b. p. $114\cdot5^\circ$, was a mixture of two forms, one crystalline, m. p. $46\cdot5^\circ$, and the other liquid, of which the latter was not obtained quite free from its isomeride. Both were interconvertible and much less stable than the two benzaldoximes but such experimental evidence as could be obtained indicated that they corresponded to the *anti*- and *syn*-aldoximes respectively. Propaldoxime and isobutaldoxime were also each separated into *anti*- and *syn*-forms (*J.*, 1892, **61**, 470; *Proc. Chem. Soc.*, 1892, 135; *J.*, 1894, **65**, 206; cf. Carveth, *J. Physical Chem.*, 1898, **2**, 159). In the period 1896—1901, in collaboration with E. Goulding, Dunstan published six papers dealing with the action of alkyl halides on hydroxylamine and on oximes. With the former, action is most complete with methyl iodide, which produces di- and tri-hydroxylamine hydriodides, and trimethylhydroxylamine hydriodide, $(\text{CH}_3)_3\text{NO}\cdot\text{HI}$, later called trimethyloxamine or trimethylamine oxide hydriodide. With ethyl, *n*-propyl, or isopropyl iodide only the dialkylhydroxylamine is formed at the first stage but the triethyl compound can be got by further action of the alkyl iodide, though this does not happen with the di-*n*-propyl and diisopropyl compounds. These trialkylated substances were the first examples of aliphatic amine oxides, and it was later found that they could be produced by the action of hydrogen peroxide on trialkylamines and that by like means dialkylamines could be converted into the dialkylhydroxylamines $(\text{Alk})_2\text{N}\cdot\text{OH}$, except in the case of dimethylamine, which instead was oxidised to formaldehyde and formic and nitrous acids (*J.*, 1896, **69**, 839; 1899, **75**, 792, 1004; 1901, **79**, 641). Also, with E. Goulding as collaborator, Dunstan investigated the action of alkyl iodides on a series of aldoximes and ketoximes alone and in presence of sodium methoxide in methyl alcohol. In the former case *N*-alkyl derivatives, then represented



as alkylisooximes, *e.g.*, the alkylisooaldoximes $\text{R}\cdot\text{CH}—\text{NR}'$, were alone formed, whereas in presence of alkali the isomeric ethers, *e.g.*, the alkylaldoximes, $\text{R}\cdot\text{CH}\cdot\text{N}\cdot\text{OR}'$, were also produced, the relative proportions of the two isomerides varying with the nature of the oxime and the alkyl iodide used (*J.*, 1897, **71**, 573; 1901, **79**, 628).

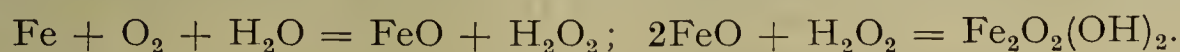
Of the remaining investigations probably the most important is that of the aconite alkaloids, on which eighteen papers were published during 1891—1905, with several collaborators, notably W. H. Ince, J. C. Umney, F. W. Passmore, F. H. Carr, H. A. D. Jowett, E. F. Harrison, T. Tickle, H. M. Read, and A. E. Andrews. The early workers on aconitine, Alder Wright in this country and Jurgens in Germany, adopted for the alkaloid the formula $\text{C}_{33}\text{H}_{43}\text{O}_{12}\text{N}$ or $\text{C}_{33}\text{H}_{47}\text{O}_{12}\text{N}$, and $\text{C}_{33}\text{H}_{45}\text{O}_{12}\text{N}$ was found by Dunstan and Ince. Up to that time aconitine had been regarded as benzoyleaconine, isomeric with the substance variously named picraconitine, isaconitine, or benzaconine. In 1892 Ehrenburg and Purfurst (*J. pr. Chem.*, 1892, **45**, 604) showed that, when heated dry, aconitine loses acetic acid, and this was later confirmed by Dunstan and Carr (*J.*, 1894, **65**, 176) who isolated and characterised the resulting pyraconitine, $\text{C}_{31}\text{H}_{41}\text{O}_{10}\text{N}$. Meanwhile Freund and Beck (*Ber.*, 1894, **27**, 433, 720) had found that the empirical formula of aconitine should be $\text{C}_{34}\text{H}_{47}\text{O}_{11}\text{N}$, which after some discussion was accepted by the English workers, and both protagonists agreed that aconitine was acetylbenzoyleaconine. It thus became the prototype of the highly toxic diacylaconines characteristic of many aconites of which *pseudoaconitine* from Nepaul aconite was shown to be acetylveratroyl*pseudoaconine* (Dunstan and Carr, *J.*, 1897, **71**, 350), *indaconitine* from *A. chasmanthum* to be acetylbenzoyl*pseudoaconine* (Dunstan and Andrews, *J.*, 1905, **87**, 1620), *bikhaconitine* from *A. spicatum* to be acetylveratroyl*bikhaconine* (Dunstan and Andrews, *ibid.*, p. 1636), and *japaconitine* from Japanese aconite to be acetylbenzoyljapaconine (Dunstan and Read, *J.*, 1900, **77**, 49). All these alkaloids and certain of their derivatives were examined pharmacologically by Professor Cash, and the detailed results

communicated to the Royal Society (Cash and Dunstan, *Phil. Trans.*, 1898, B, **190**, 239; 1902, B, **195**, 39, 97; *Proc. Roy. Soc.*, 1905, B, **76**, 468; see also Cash, *Brit. Med. J.*, 1908, I, 1213).

The series of papers on "Cyanogenesis in Plants" arose out of the poisoning of domestic animals in Egypt by *Lotus arabicus*, a plant which when fully ripe is collected by the Arabs as fodder for cattle but which had long been known to be poisonous in the early stages of growth. It was found that dried immature plants when ground and moistened with water produced a strong odour of prussic acid. This cyanogenetic action was traced to the action of an enzyme, lotase, on a glucoside, lotusin, which produced prussic acid, dextrose, and a yellow pigment, lotoflavin (Dunstan and Henry, *Phil. Trans.*, 1901, B, **194**, 515). It was not easy in those days to get collected in good condition the considerable supply of material required for chemical examination and though a fair quantity of this plant became available it arrived in small quantities, in which the yield of prussic acid varied, and the plant was sometimes mature enough to yield only traces. The total amount of lotusin obtained was small in comparison with the yield of prussic acid from dried young plants in good condition, and this deficiency is still not accounted for in the preliminary account of a re-examination of the plant started just before the outbreak of war (Henry, *J. Soc. Chem. Ind.*, 1938, **57**, 248), in which a well-defined pigment glucoside, $C_{22}H_{24}O_{11}$, was isolated along with the cyanogenetic glucoside, lotaustralin, which Finnemore, Cooper, and Stanley (*ibid.*, p. 162) first obtained about the same time from the related plant *Lotus australis* var. *pubescens*. In this second investigation in which acetone was used as the extracting medium in place of alcohol, no lotusin was isolated but the residual extracts still contained much cyanogenetic material. The second plant examined was "dhurra" (*Sorghum vulgare*) from Egypt. In this case also the toxic substance disappears as the plant matures and there is none in the seed, which is a common tropical food-grain. The cyanogenetic glucoside in this case was named "dhuririn" and proved to be a glucoside of *p*-hydroxybenzaldehyde cyanohydrin. An easier material to deal with was the seeds of *Phaseolus lunatus*, which as collected from the semi-cultivated plant, grown as a green manure in Mauritius, are brown with violet patches and poisonous, as distinct from the white and harmless "Lima beans," yielded by the carefully cultivated plant. Previous observations by Bonamé in Mauritius and by van Romburgh in Java had shown that this plant when crushed, moistened with water, and distilled yielded acetone and prussic acid. The formation of these products was traced to the action of an enzyme on phaseolunatin, which proved to be a glucoside of acetone cyanohydrin (Dunstan and Henry, *Proc. Roy. Soc.*, 1903, B, **72**, 285) which was later also isolated from cassava root and from young flax plants (Dunstan, Henry, and Auld, *Proc. Roy. Soc.*, 1906, B, **78**, 145, 152; 1907, **79**, 315), and the linamarin obtained from flax by Jorissen and Hairs (*Bull. Acad. Roy. Belg.*, 1891, [iii], **21**, 529) was shown to be identical with phaseolunatin.

Among other natural products examined mention may be made of the Egyptian plant *Hyoscyamus muticus*, which was shown to contain hyoscyamine without hyoscyne (Dunstan and Brown, *J.*, 1899, **75**, 72) and has now for many years been a commercial source of atropine.

Dunstan also made an excursion into inorganic chemistry in a group of papers on the rusting of iron, in which he maintained that the essential condition for the aerial oxidation or rusting of iron and other metals is the simultaneous presence of oxygen and liquid water, that carbon dioxide facilitates but does not initiate the process, and that agents such as alkalis, potassium dichromate, sodium nitrite, and potassium ferrocyanide, which prevented, to a greater or less extent, the formation of rust were also agents in whose presence the decomposition of hydrogen peroxide occurs, from which he deduced that hydrogen peroxide is an essential intermediary in the formation of rust and that in the case of iron the process may be represented:



Though this view (*Proc. Chem. Soc.*, 1903, **19**, 150) was supported by much experimental evidence (Dunstan, Jowett, and Goulding, *J.*, 1905, **93**, 1548) it led to considerable discussion. Up to that time the findings of Grace Calvert (*Manchester Lit. Phil. Mem.*, 1871, **5**, 104) as interpreted by Crum Brown (*J. Iron Steel Inst.*, 1888, 129), that rusting was due to the combined action of the carbon dioxide and oxygen of the air, had not been questioned and it was assumed that the iron carbonate first formed was gradually converted into a ferric hydroxide or rust by the further action of atmospheric oxygen. That theory was now supported by G. T. Moody and his notes led to interesting discussions at meetings of the Society (*Proc. Chem. Soc.*, 1903, **19**, 157, 239, 273; 1906, **22**, 101; 1907, **23**, 84; 1909, **25**, 34; *J.*, 1906, **89**, 720; cf. Dunstan, *Proc. Chem. Soc.*, 1907, **23**, 63). An electrolytic explanation of the corrosion of iron was advanced by Whitney (*J. Amer. Chem. Soc.*, 1903, **25**, 394) and received some support from Walker, Cederholm, and Bent in the United States (*ibid.*, 1907, **29**, 1251) and from Tilden in this

country (*J.*, 1908, **93**, 1356). Experimental evidence against both these theories was provided by Dunstan *et al.* (*loc. cit.*) and, in returning to the subject, Dunstan and J. R. Hill (*J.*, 1911, **99**, 1835, 1853) emphasised that "none of the existing theories adequately explains how the various inhibiting agents prevent rusting" and in the first of the two papers quoted they record the results of a number of new experiments showing that all these inhibitors act by rendering iron "passive" and that this passivity persists after removal of the iron from the solution causing it. It was also suggested that, as potassium iodide and certain other reducing agents destroy hydrogen peroxide and yet do not inhibit rusting, the peroxide is probably not an intermediate product of the main reaction as originally postulated but may be the result of a secondary reaction, since oxidation can apparently proceed without its formation, and they conclude that "metals undergo aerial oxidation by direct action of oxygen dissolved in water."

In 1899, largely under Dunstan's influence, a Research Laboratory was inaugurated by the Pharmaceutical Society, by addition to their premises in Bloomsbury Square, and most of the work referred to above was started in that institution and was transferred to, and continued in, the Scientific and Technical Department of the Imperial Institute when Dunstan moved there in 1896. The Institute was founded to commemorate the fiftieth year (1887) of Queen Victoria's reign and was opened by Her Majesty in 1893, by which time some progress had been made in installing in the Public Exhibition Galleries representative collections of the natural products of the Colonies and India, and it was possible to begin giving attention to the second objective of the Institute, the scientific examination of new or little known products from the Overseas Empire. The Institute was severely handicapped by lack of funds but the first Director, Sir Frederick Abel, found it possible to secure the co-operation of a number of eminent men of science, who undertook to examine in their own laboratories materials provided by the Institute. Much useful work was done under this arrangement, *e.g.*, by Dr. A. W. Crossley and Mr. Le Sueur on Indian vegetable oils, by Professor W. C. Unwin on mechanical tests of new timbers, by Professor A. H. Church on the composition of Indian food-grains, by Messrs. Cross and Bevan on new fibres, and by Professors A. G. Perkin and J. J. Hummel respectively on the components and the tinctorial properties of Indian dye-stuffs. This arrangement was continued when, thanks to the generous financial help provided by the Commissioners of the 1851 Exhibition, the Goldsmiths' and Salters' Companies and other donors, it was possible to equip and operate the laboratories of the Scientific and Technical Department on Dunstan's assumption of the Directorship in 1896. During the first few years it was still possible to carry on mainly detailed investigations such as those already referred to, but as the facilities offered by the Institute for the examination of natural products became better known in the Colonies and India, thanks to Dunstan's organizing ability and driving power, the character of the work done had perforce to change, as will be seen in the volume of "Technical Reports and Scientific Papers" published by the Imperial Institute in 1903, which opens with an interesting preface by Sir Frederick Abel describing the inception of the Institute and the objectives which its founders had in view. Part I of the volume is a series of reports on coals, iron ores, mica, and other minerals, followed by collected reports on fibres, edible and essential oils and oil-seeds, rubber and gutta percha, gums and resins, medicinal plants and tobacco, tanning and dyeing materials, fodder plants and food-grains, and timbers, many of the items being provided by the scheme of co-operation with the external expert referees referred to above. From 1903 the more important technical reports of the Department were published in the quarterly *Bulletin of the Imperial Institute* but in the period 1909—1914 a further group of five collected reports, with Dunstan as responsible editor and dealing with Fibres, Gums and Resins, Foodstuffs, Rubber and Gutta Percha, and Oil-seeds, Oils, Fats, and Waxes, was issued in the Miscellaneous Series of Colonial Reports. Also printed in this series was the "Report on British Cotton Cultivation," which with Dunstan's prior "Report to the Board Trade on Cotton Cultivation in the British Empire and Egypt" (1904) indicates the part played by the Imperial Institute, when, in the early years of this century, there was a prospective shortage of raw cotton and strenuous efforts were made to increase cultivation of this commodity within the Empire. In the same connection Dunstan also paid official visits to Cyprus and Asia Minor and prepared reports, published in the same series, on the agricultural resources of those areas with special reference to cotton cultivation. He was also responsible for another important development in the exploration and utilisation of Colonial natural resources, *viz.*, the institution of Mineral Surveys in Ceylon, Southern Nigeria, Northern Nigeria, and Nyasaland. These were conducted by geological surveyors operating in the territories named, and the mineral samples collected by them were sent to the Imperial Institute for mineralogical and chemical examination. Reports on this work were also published in the Miscellaneous Series of Colonial Reports. Among the more interesting results were the

discovery of thorium minerals, especially the new mineral thorianite (Dunstan, *Nature*, 1904, 69 510; with G. S. Blake, *Proc. Roy. Soc.*, 1905, A, 76, 253; with B. M. Jones, *ibid.*, 1906, A, 77, 346) in Ceylon by Dr. Coomaraswamy, the location of beds of lignite and of the now important Udi coalfield in Southern Nigeria by Mr. A. E. (later Sir Albert) Kitson, and of deposits of iron ore in Northern Nigeria by Dr. J. D. Falconer who subsequently became Director of the Geological Survey of Nigeria and is the author of a monograph on "The Geology and Geography of Northern Nigeria."

Dunstan also considered the publication of information regarding the natural resources of the Overseas Empire as an important function of the Imperial Institute, and a section of the quarterly *Bulletin* was always allocated for this purpose. This also was the idea behind three series of publications issued by Mr. John Murray, namely :

"The Imperial Institute Handbooks to the Commercial Resources of the Tropics," of which four volumes were issued with Dunstan as Editor.

"The Imperial Institute Monographs on Mineral Resources with special reference to the British Empire." Fifteen of these, each dealing with one set of minerals, were prepared under the direction of the Mineral Resources Committee of the Imperial Institute.

A series of reports on rice, lac, turpentine, oil-seeds, etc., resulting from the Indian Trade Enquiry authorised by the Secretary of State for India in 1916.

The *Bulletin of the Imperial Institute* for 1923 contains a long and detailed "Report on the Operation of the Imperial Institute," which deals with the organization and work of the Institute up to a date shortly before Dunstan's retirement. It is an interesting account of the foundation and progress of an organisation concerned with this important phase of colonial economic development, to which he devoted nearly two-thirds of his working life.

Dunstan was a Fellow of the Chemical Society for 70 years, having joined in 1879; he served on the Council in 1889 to 1891 and was Secretary from 1893 to 1903 and a Vice-President from 1904 to 1906. He became a Fellow of the Royal Society in 1893 and was a member of the Council from 1905 to 1907. He presided over the Chemical Section of the British Association at the meeting held in York in 1906. In 1910 he became President of the International Association of Tropical Agriculture, which had its headquarters in Paris, and in that capacity was President of the Third International Congress of Tropical Agriculture, held at the Imperial Institute in 1914, just before the outbreak of the First World War. He also served on the Council of the Royal Geographical Society in 1916. Dunstan was fond of travel. As already mentioned he visited Cyprus in 1904 and Asia Minor in 1907 at the request of the Colonial Office and, at the invitation of the respective governments, he undertook similar missions to Ceylon in 1910 and 1914, India in 1914, and Newfoundland in the same year.

Dunstan was an excellent lecturer and in his teaching days was always popular with his students. He was interested in education, especially in science teaching, and this led to his service as Secretary of the British Association Committee dealing with that subject from 1887 to 1891. It was also no doubt this interest which led to his serving at various times on the governing bodies of constituent colleges of London University and to his becoming a Vice-President of the Girls' Public Day School Trust.

Dunstan was also concerned with philosophy and in an article on "Our Quest for Philosophy and what came of it," contributed to the *Hibbert Journal* for July 1942, he describes his association with Dr. Alfred Senior in the foundation of the Aristotelian Society of which he was one of the first three Vice-Presidents, and for a time he edited the Society's *Proceedings*.

He was also an honorary member of the Institut Egyptien, and a Commander of the Order of Leopold of Belgium.

He was made C.M.G. in 1913 and K.C.M.G. on his retirement in 1924.

Dunstan was married twice, in 1886 to Emilie Fordyce Maclean, who died in 1893 leaving a son and a daughter, and in 1900 to Violet Hanbury-Tracy, who survives him with a second daughter.

T. A. HENRY.

